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A Chemical Amplification Method for the Polarographic Determination of Trace Amounts of Boron*

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It is shown that boron can be estimated by dc polarography at μg/ml level by using two chemical amplification reactionsin sequence. In this method, boron is converted into molybdotungstoboric acid by its reaction with ammonium molybdate and sodium tungstate under suitable conditions and is separated by solvent extraction. Determination of molybdenum in the organic extract gives an indirect estimation of boron with an enhancement factor of 6. *A further enhancement* by a factor of 44 is achieved by determining molybdenum through catalytic dc polarography in nitrate medium. With the overall enhancement factor of 240 and with the use of charging current compensation *to minimise* the background, the detection limit for boron is 0.25 μg/ml and the relative standard deviation is 5% (at 20 μg level).

We had shown earlier' that by coupling two different chemical amplification reactions in tandem, the sensitivity of dc polarography can be significantly enhanced. A sensitivity of the order of ng/ml was reported by us[2] for the indirect estimation of phosphorus, arsenic and silicon by dc polatography employing this approach in conjunction with background suppression by charging current compensation. In a later communication[3], we established that this approach could he used to estimate phosphorus, arsenic and silicon when they are present together. In,a short note' we showed that this approach dramaticahy improves the sensitivity of dc polarography for the analysis of a number of elements (phosphorus, arsenic, silicon, germanium, cerium, thorium, niobium. vanadium, boron and titanium) which all form heteropolyacids. In this paper we present the details of our study on the use of this approach for the estimation of boron.

Neither boric acid nor borates are electrochemically active and no direct polarographic methods for their determination are therefore possible. However, several indirect polarographic methods have been reported. These are based on the suppression of polarographic waves due to the reduction of benzil in sodium hydroxide solution, thenoyl trifluoro acetone, fructose, 2', 2'-dihydroxybenzoin solution and 3 nitrocatechol by boric acid or borate ions[5]. These methods suffer from poor sensitivity and selectivity. The method described here is based on the use of two different chemical amplification reactions in sequence. The first amplification reaction used here is the formation of the heteropoly acid, molybdotungstoboric acid (MTBA), which is selectively extracted. The second amplification reaction *is* the determination of molybdenum in extracted MTBA by catalytic dc polarographic wave.

Experimental Procedure

Instrumentation—The charging current compensated dc polarograph (ccc.dcp) constructed in our laboratory and reported earlier[6] was used in conjunction with a Brians X-Y recorder type 24000 A to obtain the polarograms. A water-jacketed Metrohm polarographic cell with mercury pool as counter electrode and SCE as referenceelectrode was used with a Sargent capillary having a natural drop time of 3 s as DME. Temperature was maintained at 34+ 0.1°C unless otherwise stated. Deaeration was effected by bubbling purified hydrogen through the solution for 10 min. The drop time was kept at 0.5 s by an electromechanically controlled knocker. *p*H measurements were made with a Philips digital *p*H meter, type 7100 A.

Reagents

1. Standard boron solution (10 μg/ml)—Dissolve 0.05710 g of boric acid in water and make up to 1 litre.

2. Ammonium molybddte (0.05 *M*)—Dissolve 15.45 g ammonium molybdate tetrahydrate in 250 ml water.

*Dedicated Io Professor K S *G* Doss on his eightieth birthday.

3. Sodium tungstate solution (0.05 *M*)—Dissolve 8.24 g of sodium tungstate dihydrate in 500 ml water.

4. 1:1 mixture of methyl isohutyl ketone and *n*-butanol.

Procedure—In different polythene beakers, take 0 to 5 ml aliquots of the standard boron solution. Add to each 5 ml of 0.05 *M* ammonium molybdate, 3 ml of 0.05 *M* sodium tungstate and adjust the *p*H to 1.5. Heat the solutions on a boiling water bath for about 30 min and then allow to stand at room temperature for about I h. Transfer the solutions to 125 ml separatory funnels and add 8 ml of 11 *N* sulphuric acid, dilute to 35 ml and then extract with 15 ml portions of a 1:1 mixture of hutanol and methyl isohutyl ketone by shaking for about 1 min. After the separation of phases, discard the aqueous layer and wash the organic layertwicewith 15 ml 1 *M* HCl by shaking for 30 s each time. Strip the molybdenum from the organic layer by shaking it with 10 ml of 0.5 *N* sodium hydroxide for 1 min. Collect the sodium hydroxide layer in a 50 ml standard flask, add 6.7 ml of 4.5 N H_2SO_4 and make up to the mark. Add a suitable aliquot to the polarographic cell containing 20 ml of supporting electrolyte (1 *M* sodium nitrate and 0.25 *M* sulphuric acid) and record the polarogram.

Results and Discussion

Formation *and* extraction *of MTBA*—Although boron is known to form heteropolyacid complex similar to phosphorus, arsenic and silicon, very little Work has been reported on the use of such species for quantitative boron analysis. Jean'. examined the formation of tungstoboric acid as the basis for the absorptiometric determination and concluded that due to incomplete formation of tungstohoric acid and polymerisation *of* tungstic acid, tungstohoric acid cannot be made the basis for spectrophotometric determination of boron. A solution to the problem of using MTBA for the spectrophotometric determination of boron was found by Suhha Rao[8]. Boron reacts in weakly acidic solution, withmolyhdate and tungstate to form a triple heteropoly complex'. Employing this result. optimum conditions for the formation and extraction of tungstohoric acid complex were evolved. The optimum conditions which were in agreement with those reported earlier were found to he as follows:

a. For the formation of MTBA best conditions were: 3 ml of 0.05 *M* sodium tungstate and 5 ml of 0.05 *M* ammonium molyhdate for a volume of 35 ml and a *p*H of 1.5.

b. For the extraction of MTBA optimal conditions were: an acidity of 2.5 N with respect to sulphuric acid and a volume of 15 ml of 1:1 mixture of *n*-butanol and methyl isohutyl ketone (when the aqueous phase volume is 35 ml).

c. Forwashingtheorganiclayerthebestreagent was 1 *M* HCl.

d. For the quantitative stripping of molybdenum from the organic phase the best reagent was 10 ml of 0.5 *N* sodium hydroxide.

The stoichiometry is found to be 1:6:6 for B:Mo:W in MTBA complex. Hence direct determination of Mo in the extracted MTBA would increase the sensitivity because 6 molybdenum atoms per boron atom become available for measurement.

Estimation *of* molybdenum by *catalytic dc* polarography—Catalytic currents are given by molybdate in perchlorate, nitrate and chlorate solutions. Though some arguments still remain about the species involved in the catalysis, they can he employed for analytical purposes, if the catalytic waves are well defined and reproducible'. Catalytic waves obtained from nitrate medium satisfy these criteria. We found that it was best to use a supporting electrolyte *of* concentration 1 *M* sodium nitrate and 0.25 *M* sulphuric acid as reported in earlier[2,3]

Interference—It is known that tungstate gives a catalytic wave[9]. Since MTBA contains tungsten, the possible interference of tungstate in the polarographic determination of molybdate was investigated in detail. Fig. I shows the dc polarograms of tungstate in 0.25 *M* sulphuric acid and 1.*M* sodium nitrate supporting electrolyte. No tungstate wave could he seen at 24.7 μg/ml level, wheteas at a tungstate concentration of 48 μg/ml level, the appearance of a small drawn out wave could be seen. In the same figure is also shown the wave of 0.245 μg/ml molyhdate. From a comparison of the wave heights of molybdenum and tungsten, it is

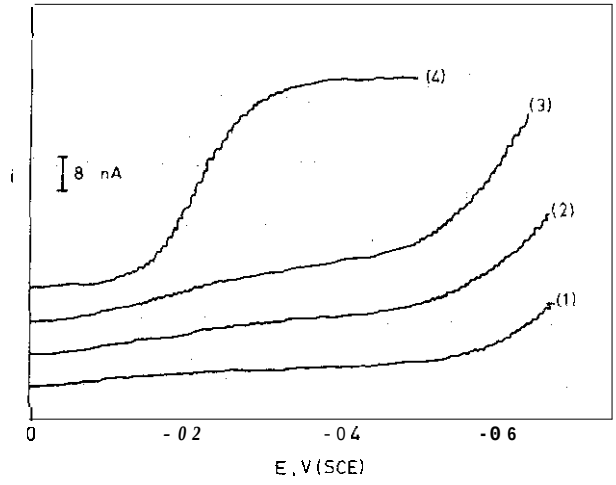

Fig. 1—Polarograms of (1) supporting electrolyte alone; (2) 24.7 μg/ml tungslate in (1); (3) 48.2 μg/ml lungstate in (I); (4) For a comparison 0.245 μg/ml molybdate in (I)

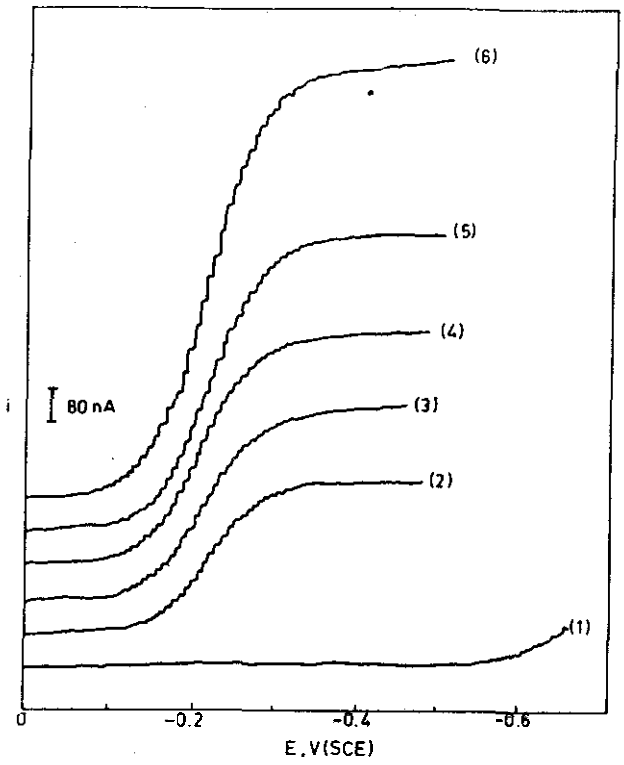

Fig. 2—Various polarograms which were used for the construction of the calibration graph for the determination of boron: (1) supporting electrolyte alone; (2) to (6) polarograms of stripped molybdenum equivalent to- (2) 0 μg/ml boron; (3) 0.1 μg/ml boron; (4) 0.29 μg/ml boron; (5) 0.48 μg/ml boron and (6) 0.96 μg/ml boron

deduced that the molybdenum wave is 2280 times larger than that of tungsten. Hence for all practical purposes it can be concluded that tungsten does not interfere in the determination of molybdenum. However, in the formation and extraction of MTBA, phosphorus, arsenic and silicon were found to exert a positive interference. This can be avoided by a prior separation of boron by a suitable method.

Sensitivity and detection limit—Fig. 2 shows the various polarograms which were used to construct the calibration graph for the determination of boron and Fig. 3 the actual calibration graph obtained by this method. Taking the slope of the calibration graph as a measure of sensitivity, it is seen that the method offers a sensitivity of 8 nA/ppb. Defining detection limit as that concentration which gives a signal twice as much as the random noise, we find that for the instrument we have used it is 1 ppb. However in this study we find that the detection limit for boron estimation that could be realised in practice by the procedure described here is 0.25 μg/ml. This difference in detection limit is due to the simultaneous extraction of isopoly molybdate which is present in significant amounts in the system

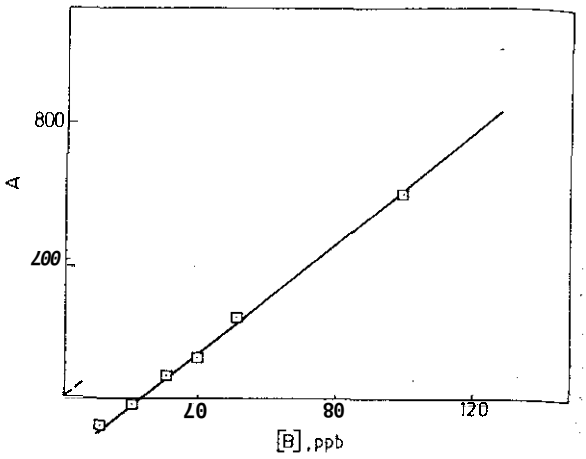

Fig. 3—Calibration graph for the estimation of boron

due to the polymerisation of ammonium molybdate. The relative standard deviation for the method is 5% (when 20 μg is taken for analysis and 1 ml is added to polarographic cell).

Conclusion

It is shown here that by combining two different chemical amplification reactions in sequence it is possible to improve the sensitivity of a conventional analytical method, viz. dc polarography, to that of a trace analytical method. In this communication a highly sensitive polarographic method has been reported for boron employing the above approach. The proposed method happens to be one of the few satisfactory polarographic methods available for the determination of boron.

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